A COMPARATIVE STUDY OF EFFECTS ON CHARACTERISTIC PROPERTIES OF FRP COMPOSITES WHEN EXPOSED TO DISTILLED WATER, NaCl- WATER SOLUTION AND SEA WATER SEPARATELY

A THESIS SUBMITTED IN PARTIAL FULFILLMENT
OF THE REQUIREMENT FOR THE DEGREE OF

Bachelor of Technology
in
Metallurgical and Materials Engineering

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Department of Metallurgical and Materials Engineering
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Under the Guidance of
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CERTIFICATE

This is to certify that the thesis entitled, "**A COMPARATIVE STUDY OF EFFECTS ON CHARACTERISTIC PROPERTIES OF FRP COMPOSITES WHEN EXPOSED TO DISTILLED WATER, NaCl-WATER SOLUTION AND SEA WATER SEPARATELY**" submitted by Sri DIPAK KUMAR PATEL & SHUBHONIL BANERJEE in partial fulfillment of the requirements for the award of Bachelor of Technology Degree in Metallurgical and Materials Engineering at the National Institute of Technology, Rourkela (Deemed University) is an authentic work carried out by him under my supervision and guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University / Institute for the any Degree or Diploma.

Date:

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Dipak Kumar Patel
Shubhonil Banerjee

CONTENTS

ABSTRACT

A comparative study of effects on characteristic properties of FRP composites when exposed to Distilled water, NaCl- water solution and sea water separately was done. Composite of E- glass fiber reinforced in epoxy resin (araldite LY556) in 40:60 weight ratios was used. Samples were immersed for 2, 4, and 8 days in the three mediums separately at 60˚C and 95% humidity in a humid chamber. ILSS values were calculated using INSTRON 1195. It was found that all solutions marginally degraded the mechanical property this was mainly the result of polymer hydrolysis. The diffusivity was found to be maximum in case of 3.2% NaCl solution and minimum in sea water. The immersion in sea water had least affect on mechanical properties. As evidenced by SEM micrographs, the worst case of damage involved large amount of debonding and fiber pullout in case of 3.2% NaCl solution, while sea water least affecting the matrix.

Keywords: Epoxy resin, Glass fiber reinforced plastics, sea water, ILSS, moisture gain, Distilled water, glass transition temperature.

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Chapter 1

INTRODUCTION

INTRODUCTION

Many of our modern technology require materials with unusual combinations of properties that cannot be met by the conventional materials such as metals, alloys, ceramics and polymers etc. The need for the polymeric composites has been much felt in the offshore oil industry, submarine and ship building industry, as they offer the advantage of chemical stability and, by and large, are not susceptible to aqueous corrosion. These are increasingly used in civil infrastructure renewal applications, off-shore platforms, oil development-related structural facilities and marine infrastructure.

In all the above use, the FRP composite is exposed to moisture coupled with other chemicals. The deterioration that occurs in FRP during the service life in general, is linked to the level of moisture that is absorbed. It may be possible that the presence of moisture in the composites, whether by itself or in combination with other chemicals, can initiate undesirable structural changes within the fiber reinforcement and the matrix or the interface between the two. The absorption of moisture may cause plasticization of the resin to occur with a concurrent swelling and lowering the glass transition temperature of the resin. This may adversely affect the fiber matrix adhesion properties, resulting debonding at fiber/matrix interfaces, micro-cracking in the matrix, fiber fragmentations, continuous cracks and several other phenomena that may actually degrade the mechanical property of the composites. The reduction in the glass transition temperature makes the polymer soft and it can enhance creep deformation. The water ingress is the increase in volume or swelling of the sample, and this can induce stresses similar to thermal responses that could cause micro cracks.

In spite of these studies, there are several gaps in our knowledge of this subject: for example, the interlaminar shear strength, which is an important design parameter, has not received much attention from this point of view. Secondly, though the effect of water absorption has received considerable attention, the effect of salt and sea water has received only a little attention. This effect has become increasingly important due to marine applications of the glass fiber reinforced plastics (GFRP).

All the above phenomena have been reported in literature. From the viewpoint of maintaining or enhancing durability of a particular GFRP system, it is essential to know which of these effects is likely to be dominant under which set of conditions, thus we would be able to

(i) Avoid the possibility of occurrence of any premature fracture.

(ii) Devise methods of strengthening the structure.

Chapter 2

WHY WE TOOK UP THIS WORK?

2. Why We Have Taken Up This work?

The basic reason for working on such a topic arises from the fact that composites are vulnerable to environmental degradation. A moist environment, coupled with high or low temperature conditions is extremely detrimental for composites.

The need for polymeric composites has been much felt in offshore oil industry, submarine and ship building industry, and as composites have to sustain long hours of warm moist saline environments there, it is important to understand how sea water environment affects the mechanical properties of the composites

Innumerable studies on composites conditioned in moist environments were carried out on the rates and levels of absorption, and the consequent degradation in their mechanical properties. The motivation of our study is different mechanisms of material degradation may occur in different atmosphere and different salts may have different effect.

In our project we will do a comparative study of the effects on characteristic properties of FRP composites when exposed to distilled water, NaCl water solution and sea water separately. We will make a comparative study of the effects of immersion of the composite in distilled water, NaCl solution and sea water and experimentally try to analyze the effect of the immersion in the different mediums basing on the experimental data. The ILSS values obtained from the 3 point bend test, the water pick up will be measured and finally the mode and cause of failure will be studied.

Chapter 3

LITERATURE REVIEW

3. LITERATURE REVIEW

3.1 COMPOSITES

A composite is combination of two materials in which one of the materials, called the reinforcing phase, is in the form of fibers, sheets, or particles, and is embedded in the other materials called the matrix phase. The reinforcing material and the matrix material can be metal, ceramic, or polymer. Composites are used because overall properties of the composites are superior to those of the individual components. For example: polymer/ceramic composites have a greater modulus than the polymer component, but aren't as brittle as ceramics. The following are some of the reasons why composites are selected for certain applications:

- High strength to weight ratio (low density high tensile strength)
- High creep resistance
- High tensile strength at elevated temperatures
- High toughness

Typically, reinforcing materials are strong with low densities while the matrix is usually a ductile, or tough, material. If the composite is designed and fabricated correctly, it combines the strength of the reinforcement with the toughness of the matrix to achieve a combination of desirable properties not available in any single conventional material. The downside is that such composites are often more expensive than conventional materials. Examples of some current application of composites include the diesel piston, brake-shoes and pads, tires and the Beech craft aircraft in which 100% of the structural

components are composites. The strength of the composite depends primarily on the amount, arrangement and type of fiber (or particle) reinforcement in the resin. Typically, the higher is the reinforcement content, the greater is the strength. In some cases, glass fibers are combined with other fibers, such as carbon or aramid (Kevlar29 and Kevlar49), to create a "hybrid" composite that combines the properties of more than one reinforcing material.

Three types of composites are:

- Particle-reinforced composites
- Fiber-reinforced composites
- Structural composites

3.2 FIBER-REINFORCED COMPOSITES:

Reinforcing fibers can be made of metals, ceramics, glasses, or polymers that have been turned into graphite and known as carbon fibers. Fibers increase the modulus of the matrix material. The strong covalent bond along the fiber's length gives them a very high modulus in this direction because to break or extend the fiber the bonds must also be broken or moved. Fibers are difficult to process into composites which makes fiber reinforced composites relatively expensive. Fiber-reinforced composites are used in some of the most advanced, and therefore most expensive, sports equipment, such as a time-trial racing bicycle frame which consists of carbon fibers in a thermoset polymer matrix. Body parts of race cars and some automobiles are composites made of glass fibers (or fiberglass) in a thermoset matrix.

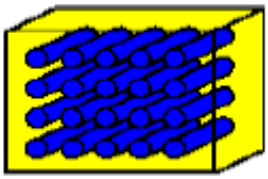


Fig 3.1 Schematic diagram of FRP Composite

The arrangement or orientation of the fibers relative to one another, the fiber concentration, and the distribution all have a significant influence on the strength and other properties of fiber-reinforced composites. Applications involving totally multidirectional applied stresses normally use discontinuous fibers, which are randomly oriented in the matrix material. Consideration of orientation and fiber length for particular composites depends on the level and nature of the applied stress as well as fabrication cost. Production rates for short-fiber composites (both aligned and randomly oriented) are rapid, and intricate shapes can be formed which are not possible with continuous fiber reinforcement.

3.2.1 TYPES OF FIBERS USED IN FIBER REINFORCED COMPOSITES:

1. Glass fibers
2. Carbon fibers
3. Aramid fibers

1. Glass Fibers

The most common reinforcement for the polymer matrix composites is a glass fiber. Most of the fibers are based on silica (SiO_2), with addition of oxides of Ca, B, Na, Fe, and Al. The glass fibers are divided into three classes --

E-glass, S-glass and C-glass. The E-glass is designated for electrical use and the S-glass for high strength. The C glass is for high corrosion resistance, and it is uncommon for civil engineering application. Of the three fibers, the E-glass is the most common reinforcement material used in civil structures. It is produced from lime-alumina borosilicate which can be easily obtained from abundance of raw materials like sand. The glass fiber strength and modulus can degrade with increasing temperature. Although the glass material creeps under a sustained load, it can be designed to perform satisfactorily. The fiber itself is regarded as an isotropic material and has a lower thermal expansion coefficient than that of steel.

1.1. ***E-glass*** *(electrical)*

Family of glassed with a calcium aluminum borosilicate composition and a maximum alkali composition of 2%. These are used when strength and high electrical resistivity are required.

1.2. ***S-glass*** *(tensile strength)*

Fibers have a magnesium aluminosilicate composition, which demonstrates high strength and used in application where very high tensile strength required.

1.3. *C-glass* *(chemical)*

It has a soda lime borosilicate composition that is used for its chemical stability in corrosive environment. It is often used on composites that contain or contact acidic materials.

Composition of E-Glass

Constituent	Weight percentage
SiO2	54
Al203	14
CaO+MgO	12
B2O3	10
Na2O+K2O	Less than 2
Impurities	Traces

Table 3.1 Composition of E-glass

3.2.2 EPOXY RESIN

Epoxy or **poly-epoxide** is a thermosetting epoxide polymer that cures (polymerizes and crosslinks) when mixed with a catalyzing agent or "hardener". Most common epoxy resins are produced from a reaction between epichlorohydrin and bisphenol-A. The

applications for epoxy based materials are extensive and include coatings, adhesives and composite materials such as those using carbon fiber and fiberglass reinforcements, (although polyester, vinyl ester, and other thermosetting resins are also used for glass-reinforced plastic). The chemistry of epoxies and the range of commercially available variations allow cure polymers to be produced with a very broad range of properties. In general, epoxies are known for their excellent adhesion, chemical and heat resistance, good to excellent mechanical properties and very good electrical insulating properties, but almost any property can be modified (for example silver-filled epoxies with good electrical conductivity are widely available even though epoxies are typically electrically insulating).

3.3 MOISTURE ABSORPTION

The moisture absorption usually takes place in presence of thermal and moisture gradients. The atoms migrate from region of higher concentration to that of lower concentration. The rate of diffusion increases rapidly with the rise in temperature. The concentration gradient of moisture is developed due to the non-uniform distribution of moisture. The presence of imperfections and internal stresses also accelerates the process of diffusion. Epoxy resin absorbs water from the atmosphere from the surface layer reaching equilibrium with the surrounding environment very quickly followed by diffusion of water into all the material. The water absorbed is not usually in liquid form but consists of molecules or group of molecules linked by hydrogen bonds to the polymer.

Water absorption is an important parameter in the degradation of polymer composites.

The gain of the water content enhances the probability of material degradation which generally follows three main mechanisms:

- Direct diffusion of water molecules through the matrix and, in some cases, through the fibers.
- Capillary flow of water molecules along the fiber/ matrix interface followed by diffusion from the interface into the bulk resin. This is a consequence of debonding mechanisms between the fibers and matrix caused by water attack at the interface.
- Diffusion through micro-cracks, pores, defects in the material.

In many cases water absorption obeys Fick's 2nd Law and diffusion is driven by the moisture concentration gradient between the environment and material producing continuous absorption until saturation is reached.

The Fickian diffusion process is influenced mainly by two factors:

(a) The internal (fiber volume fraction and its orientation)

(b) The external (relative humidity and temperature).

Percentage moisture gain was determined as:

$$\%M = \frac{\text{(Weight of treated specimen – Weight of dry specimen)}}{\text{(Weight of dry specimen)}} \times 100$$

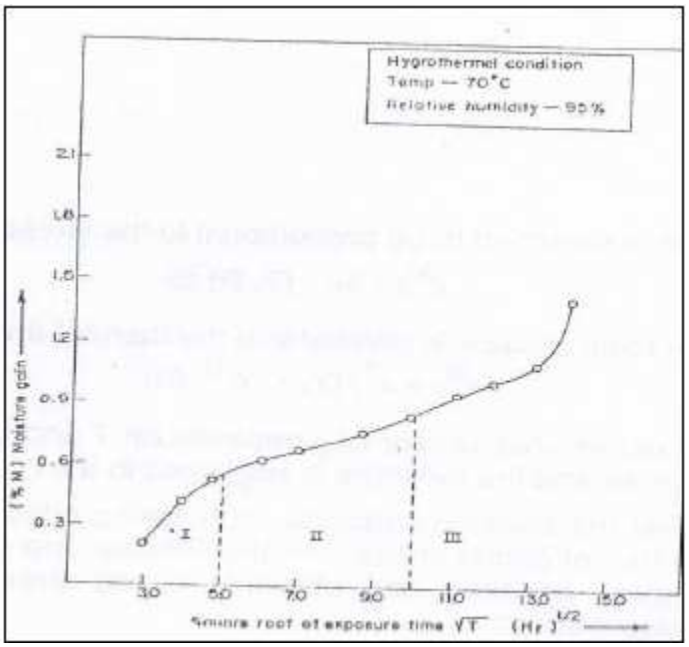


Fig 3.2 Moisture absorption kinetics

Description of the different stages in moisture absorption kinetics:

_ **Stage 1**: Moisture absorption is Fickian**.**

_ **Stage 2:** There is a deviation from linearity with the time axis (reaching saturation, so decrease in slope).

_ **Stage 3:** Total non-Fickian pattern (there is a development of micro cracks which enable rapid moisture diffusion, so rapid increase in percentage of moisture).

Non-Fickian behaviour:

Fickian behaviour is observed in the rubbery state of polymers but often fails to diffusion behaviour in glassy polymers. The deviation from Fickian behaviour occurs when:-

(a) Cracks or delamination develops.

(b) Moisture diffusion takes place along the fiber matrix interface.

(c) Presence of voids in the matrix.

The nature of diffusion behavior whether Fickian or non Fickian depends on the relative rate at which the polymer structure and the moisture distributions change. When the diffusion rates are much slower than the rate of relaxation, the diffusion has to be Fickian. Non Fickian behaviour pertains to the situations when the relaxation processes progress at a rate comparable to the diffusion process. Moisture absorption in polymeric composites is mostly Fickian type, but non-Fickian behaviour is also common for glass/epoxy composite. Absorbed moisture in the composite certainly deteriorates the matrix dominated properties but he effect is more pronounced at higher temperatures and at lower strain rates. The ILSS values are the worst affected property due to this moisture absorption.

3.3.1 Nature of water absorption in epoxy resin

Epoxy resins are commonly used as adhesives, coatings and in composites materials. They have good combination of chemical, thermal, electrical and mechanical properties but in many applications they have the disadvantage of absorption of water because of the large amount of polar OH groups in the structure which is susceptible to the polar water molecules. Absorption of water in epoxy resins leads to plasticization, the hydrolysis reactions(scission of polymer chains) and this causes decrease in the glass transition temperature Tg (it is reported that for every 1% absorption of moisture there is decrease of 20°C), swelling stresses may be generated.[4,3**].** Diffusion of water was studied in many epoxy resin in which in addition of plasticization double bonds has also been seen in which double bond acting as a physical crosslink which causes increase of Tg in epoxy resins. But it is not evident that after how long period of sorption water molecule can

form double hydrogen bonds. On the contrary it has been found that in the initial stage of sorption experiments, water molecules with double hydrogen bonds were generally observed in different epoxy systems **[**4, 8]. The water sorption at the interface shows a dual nature. The water may be present as free molecule or in combined form by forming double hydrogen bond with the hydrophilic group of epoxy resins. The formation of double hydrogen bond is clear from the following diagram:

$$H-O-H + P_1 \text{ (polar group 1)} = H-O-H\cdots P_1$$

($\cdots$ represents hydrogen bond)

Open a new polar group P_2 (polar group 2)

$$\begin{cases} \text{diffusion of water molecular from } P_1 \text{ to } P_2 \\ P_1\cdots H-O-H\cdots P2 \end{cases}$$

(water molecular with double hydrogen bonds)

$$H-O-H + P_2 = H-O-H\cdots P_2$$

A second system that has been studied extensively because of its technical importance is the adhesion between epoxy resins and glass, particularly glass fibres. To improve the hydrolytic stability of the composite, the glass surfaces are normally modified by covering them with a thin layer of a silane adhesion promoter. These silanes are well known to self-assemble into monomolecular and multi-molecular layers on surfaces such as glass or silicon dioxide. One end of the silane molecule typically has di or tri methoxy or ethoxy functionality whilst the other end normally has amine or epoxy functionality. The ethoxy functionality is believed to condense with the hydroxyl functionality on the surface of the glass whilst the amine functionality can react with the epoxy, as shown in

Fig3. 3. Hence it is attractive to suggest a simple picture of a single molecular layer of silane adhesion promoter between the epoxy and the glass. However the real situation is much more complex. The amount of silane typically used is much too great to form a monolayer. Also as the silane has multi methoxy or ethoxy functionality it can self condense. The relatively thick layer of silane is believed to form a network and then the epoxy both mixes into and reacts with the network. Although it is clear that the silane causes covalent bonding between the glass and the epoxy, there is no way to estimate the actual density of coupling produced. It is interesting to note that fairly good adhesion can be obtained in dry conditions without the silane, however it has a profound effect on adhesion in the presence of water.

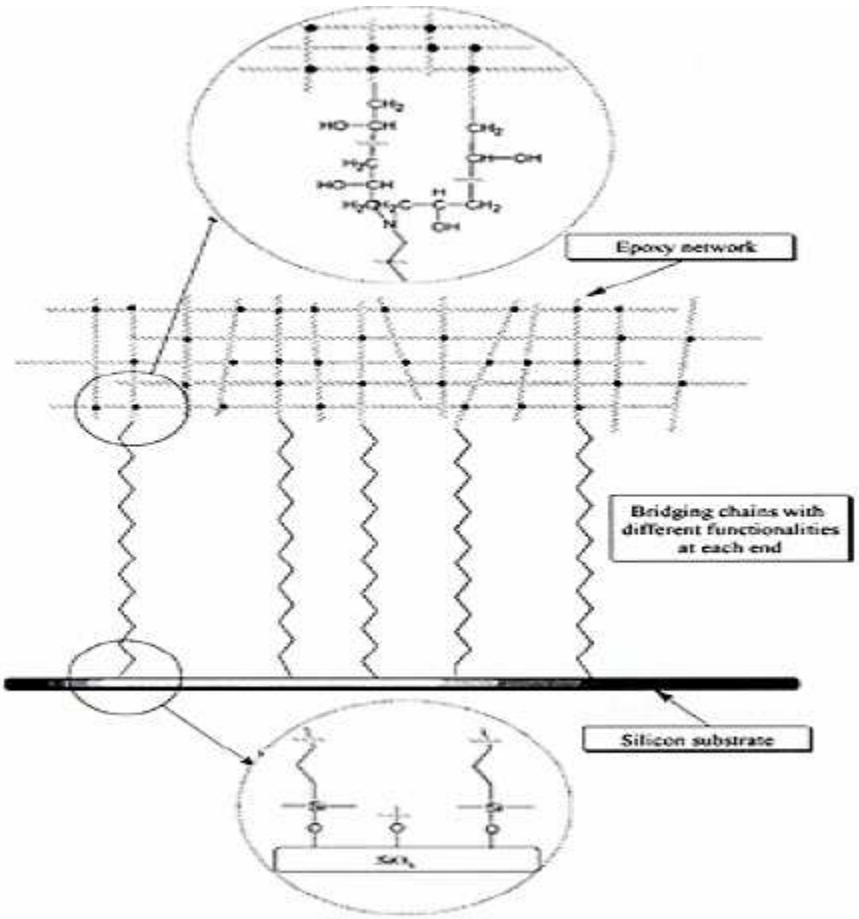


Fig 3.3 The way bridging chains, with silane functionality at one end and amine functionality at the other, can form covalent links between an epoxy network and glass substrate.

Moisture absorption is a matrix dominating property in fibre reinforced polymer composites. The fibre plays a role as much as the interface region between the fibre and the matrix may be of deferent network structure to that of the bulk matrix away from the fibre. This leads to the composite absorbing different amount of penetratefect (i.e. water) per unit mass of resin than the bulk polymer. The process of moisture absorption into the GRFP and CRFP is often considered to be driven by simple Fickian diffusion.

3.3.2 Effect of moisture absorption on FRP's properties:

It is now well known that the exposure of polymeric composites in moist environments, under both normal and sub-zero conditions, leads to certain degradation of its mechanical properties which necessitates proper understanding of the correlation between the moist environment and the structural integrity. For their several significant advantages, the composites structures are fast gaining their popularity as an effective structural component over their metallic counterparts. It is well known that there is a degradation of material property during its service life, as it is often subjected to environments with high temperature and humidity or having a sharp rise and fall of temperature (thermal spikes). The deterioration that occurs is FRP during the service life is in general, linked to the level of moisture that is absorbed. The absorption of moisture can be attributed largely to the affinity for moisture of specific functional groups of a highly polar nature in the cured resin. The absorption of moisture causes plasticization of the resin to occur with a concurrent swelling and lowering the glass transition temperature of the resin. This adversely affects the fiber matrix adhesion properties, resulting debonding at fiber/matrix interfaces, micro-cracking in the matrix, fiber fragmentations, continuous cracks and several other phenomena that actually degrades the mechanical property of the composites.

3.3.3 Effect of NaCl on moisture absorption:

In NaCl solution, two mechanisms can be imagined as contributing towards the overall hygrothermal effects on the reinforced plastics. Firstly, at the macroscopic level, the

expansion of the matrix due to absorption of water may cause tensile stresses in the fibers and compressive stresses in the matrix which is similar to differential thermal expansion. Secondly, at the molecular level, the diffusing molecules of water and sodium chloride may strain or rupture the intermolecular bond in the matrix and at the interface. In the unreinforced resin the microscopic damage is the only possible mechanism and in the reinforced plastics also this mechanism predominates because the fibers are much stiffer than the matrix. However, comparatively higher reduction in the compressive strength of the composite can be attributed to the hydroexpansion.

It has been found that there is either preferential diffusion of NaC1 molecules or that the presence of salt creates an additional capacity in the specimen to accommodate more water. This aspect is presently under investigation. [3] (S. K. Rege, S. C. Lakkad)

3.3.4 Effect of sea water on FRP's:

Seawater degradation can cause swelling and plasticisation of the polyester matrix and debonding at the fiber/matrix interface that may reduce the mechanical properties. Moisture absorption depends on the concentration of salt, the higher salt concentration produces a lower change in moisture absorption.

Changes in mechanical properties of the composite material as a consequence of fluid ingress may be reversible, partially reversible, irreversible, or a combination of these types depending on the exposure time and conditions [6, 6]. For the reversible process which involves plasticization and swelling of the polymer matrix, the mechanical properties can usually be restored by drying [6, 6]. In the case of irreversible processes

resulting in damage to the fibers, matrix cracking, debonding of the fiber/matrix interphase region, and delamination caused by swelling and/or internal stress generation, the mechanical properties are permanently altered. Damage of glass fibers by fluids is initiated by physical or chemical reactions between the two. The extent of damage depends on fluid type, fluid concentration, as well as the composition of the fibers under attack. It is now well understood that the strength of glass fiber degrades upon exposure to corrosive fluids [6,15–17]. Metcalfe and Schmitz [6,16] suggested that the underlying mechanisms of stress corrosion is driven by the exchange of alkali metal ions (Na1 and K1) in the glass and hydrogen ions (H1) of the attacking fluid. Michalske and Frieman [6, 17] have proposed a molecular model for stress corrosion of glasses and ceramics in which the silicate network (Si– O–Si bond) is destroyed by water molecules. Vauthier et al. [6, 18] showed that more broken fibers were found in environmentally aged GFRP samples than those without aging, implying degraded in situ fiber strength by aging.

3.3.5 Effect of moisture absorption on glass transition temperature

Glass transition temperature (Tg) of thermoset matrix in composites is very important property because it defines the critical service temperature of the component and consequently their applications. For practical applications they are used at a temperature below their Tg i.e. in the glass state. When materials are exposed to hydrothermal environment, the Tg usually decreases and therefore, the service temperature of the material changes. Moisture absorption by epoxy matrix composites has plasticizer effect, as reduction of Tg of the matrix. This effect is usually reversible when water is removed but exposure to high temperature can produce irreversible effects, which is attributed to

the chemical degradation of the matrix and attack on the fiber/matrix interface. This causes increase of internal voids of the entangling polymer chain, promoting chain expansion and the micro-cracks formation into the polymer matrix [4, 14].

There are many factors on which moisture absorption depends such as temperature, fiber volume fraction, reinforcement orientation, fiber nature (i.e. permeability, polarity, and density), and area of exposed surfaces, diffusivity and surface protection.

3.4 Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) is a technique for measuring the energy necessary to establish a nearly zero temperature difference between a substance and an inert reference material, as the two specimens are subjected to identical temperature regimes in an environment heated or cooled at a controlled rate. There are two types of DSC systems in common use. In power compensation DSC (Fig. 3.4) the temperatures of the sample and reference are controlled independently using separate, identical furnaces. The temperatures of the sample and reference are made identical by varying the power input to the two furnaces.

In heat-flux DSC (Fig 3.5), the sample and reference are connected by a low-resistance heat-flow path (a metal disc). The assembly is enclosed in a single furnace. Enthalpy or heat capacity changes in the sample cause a difference in its temperature relative to the reference; the resulting heat flow is small compared with that in differential thermal analysis (DTA) because the sample and reference are in good thermal contact. The

temperature difference is recorded and related to enthalpy change in the sample using calibration experiments.

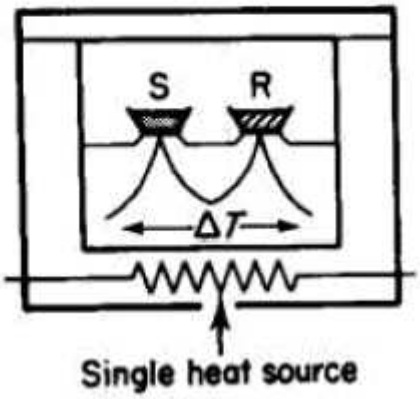


Fig 3.4 Heat flux DSC

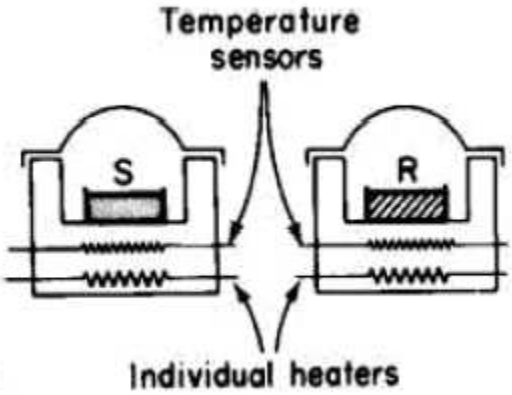


Fig 3.5 Power Compensated DSC

3.5 Scanning Electron Microscope

The Scanning Electron Microscope (SEM) is a microscope that uses electrons rather than light to form an image. There are many advantages to using the SEM instead of a light microscope. The SEM has a large depth of field, which allows a large amount of the sample to be in focus at one time. The SEM also produces images of high resolution, which means that closely spaced features can be examined at a high magnification. Preparation of the samples is relatively easy since most SEMs only require the sample to be conductive. The combination of higher magnification, larger depth of focus, greater resolution, and ease of sample observation makes the SEM one of the most heavily used instruments in research areas today.

In a typical SEM, electrons are thermionically emitted from a tungsten or lanthanum hexaboride (LaB_6) cathode and are accelerated towards an anode; alternatively, electrons can be emitted via field emission (FE). Tungsten is used because it has the highest melting point and lowest vapor pressure of all metals, thereby allowing it to be heated for electron emission. The electron beam, which typically has an energy ranging from a few hundred eV to 100 keV, is focused by one or two condenser lenses into a beam with a very fine focal spot sized 1 nm to 5 nm. The beam passes through pairs of scanning coils in the objective lens, which deflect the beam horizontally and vertically so that it scans in a raster fashion over a rectangular area of the sample surface. When the primary electron beam interacts with the sample, the electrons lose energy by repeated scattering and absorption within a teardrop-shaped volume of the specimen known as the interaction volume, which extends from less than 100 nm to around 5 μm into the surface, The size of the interaction volume depends on the beam accelerating voltage, the atomic number of the specimen and the specimen's density. The energy exchange between the electron beam and the sample results in the emission of electrons and electromagnetic radiation which can be detected to produce an image.

Chapter 4

EXPERIMENTAL PROCEDURE

4. EXPERIMENTAL PROCEDURE

Now we will focus on the experimental procedure carried out during the course of our project work. The steps carried by us were as follows:-

1. Specimen Fabrication (Fabrication of FRP).

• By Hand Lay-Up method.

• Cutting of Laminates into samples of desired dimensions.

2. Hydrothermal treatment.

3. 3-Point Bend test.

4. Characterization using DSC.

5. SEM of fractured surface.

4.1 FABRICATION OF FRP

The composite was fabricated using the conventional ***HAND LAYOUT*** method. The materials used are E-glass Fiber and Epoxy resin (araldite LY556). The hardener used is HY951. A sixteen layered structure was formed as per the ASTM standards. The fiber and the matrix were taken in the ratio of 40:60. The sample was left for drying for 24 hrs after the fabrication so that the matrix completely seeps in and become dry.

4.1.1 CUTTING OF LAMINATES INTO SAMPLES OF DESIRED DIMENSIONS

A diamond cutter was used to cut each laminate into smaller pieces, each having dimensions of 50 mm x 10 mm and thickness same as that of the laminate. This was done in accordance with ASTM standards.

4.2 HYDROTHERMAL TREATMENT

Hydrothermal treatment was carried out in HUMID CHAMBER. The 54 samples that were obtained were divided into 3 groups of 18 samples each.

- Three chambers having distilled water , 3.2% of NaCl solution and sea water are taken
- 18 samples were immersed in each chamber.

Fig 4.1 Humidity Chamber

- 6 samples were taken out subsequently after 2, 4 and 8 days from each of the chambers having distilled water, 3.2% NaCl solution and sea water respectively.
- Moisture content of every sample was measured with respect to dry weight.
- During the course of the experiment the hygrothermal chamber was maintained at 60˚C with humidity 95%.

4.3 CURING OF THE SAMPLES

- 2 Samples from each of the chambers having distilled water , 3.2% NaCl solution and sea water after 2, 4 and 8 days respectively were taken and dried in the furnace to remove any physically associated moisture at 45˚C to get a constant weight.
- The weight found was compared with the initial weight of the samples to find the weight retained in the samples.
- The samples were than subjected to 3-point bent test to find the ILSS value.

4.4 3-POINT BEND TEST

- Out of the 6 samples 4 were wiped clean and subjected to 3 point bend test in INSTRON-1195 for the measurement of ILSS in each case(as ILSS is the property which gets most effected due to moisture absorption and has been held as a criterion for measuring the effect of moisture in FRP's) 4 samples have been taken to increase accuracy
- The remaining 2 samples which were dried in the furnace to remove any physically associated moisture at 45˚C, and then subjected to 3 point bend test. The crosshead speed used was 2 mm/ minute.

The Inter Laminar Shear Stress values were then calculated for each of the specimens as follows:

ILSS = 0.75 * P/ (W * T)

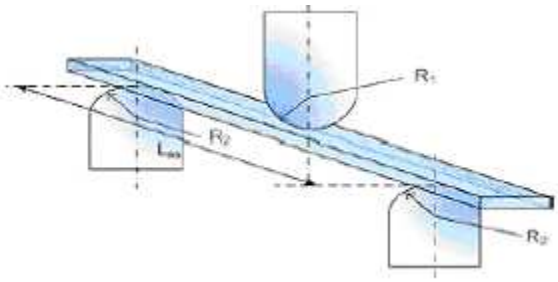


Figure 4.1 3-Point Bending Test Setup

Where

P = Breaking load

W = Width of the specimen

T = Thickness of the specimen.

4.5 CHARACTERIZATION USING DSC

The samples immersed in distilled water, sea water and 3.2% NaCl solution were put into the Differential Scanning Calorimeter. In order to calibrate the heat flow signal, a blank run with an empty pan on the reference side, and an empty pan plus a lid on the sample side, was performed before the sample measurements. Standard aluminium pans were used. The sample mass was slightly more than 10 mg. We get a curve for heat flow versus time. We get the Glass Transition temperature from those curves for each of the specimens.

4.6 SEM FRACTROGRAPHY

Scanning electron microscopy (SEM) was carried out on the fractured surface of each kind of specimens (Distilled Water, Sea Water and 3.2% NaCl Solution). One focus was done on the matrix part and the other was done on the fiber part.

Fig 4.2 Scanning Electron Microscope

Chapter 5

RESULTS, DISCUSSION & INTERPRETATION

5. RESULTS, DISCUSSIONS AND INTERPRETATIONS

FRP composites consist of fiber and matrix. The mechanical behavior or performance of the composite is determined by the local response of the fiber matrix. There is load transfer from fiber to fiber through the matrix. The region including the contact region between matrix & fiber and extending on both sides, and having some finite thickness called as interphase. The interphase possesses unique properties to the bulk matrix. It can include impurities unreacted polymers components, non polymerized additives etc. the thickness and properties of this interphase have crucial impact on the composite properties. Apart from allowing the load transfer between fibers through matrix, interphase provides a match of chemical & thermal compatibility between the constituents.

Below are the variations of moisture content with time for different mediums.

5.1 VARIATION OF MOISTURE CONTENT WITH TIME

TABLE 5.1 SAMPLES IMMERSED IN DISTILLED WATER

SPECIMEN NO:	NO. OF HOURS DISTILLED WATER IMMERSION (hrs.)	INITIAL WEIGHT (gm)	FINAL WEIGHT (gm)	% MOISTURE ABSORBED	Avg. % MOISTURE ABSORBED
1	48	6.04	6.07	0.497	0.512
2		6.46	6.49	0.464	
3		5.94	5.97	0.505	
4		6.86	6.90	0.583	
5	96	6.40	6.44	0.625	0.641
6		6.38	6.42	0.627	
7		6.20	6.24	0.645	
8		5.98	6.02	0.669	
9	192	5.95	6.00	0.840	0.820
10		6.22	6.27	0.804	
11		6.29	6.34	0.795	
12		5.94	5.99	0.842	

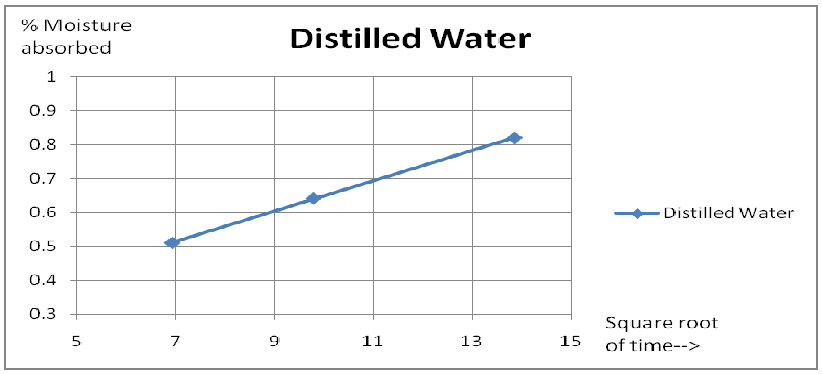
TABLE 5.2 SAMPLES IMMERSED IN SEA WATER

SPECIMEN NO:	HOURS OF SEA WATER IMMERSION (hrs.)	INITIAL WEIGHT (gm)	FINAL WEIGHT (gm)	% MOISTURE ABSORBED	Avg. % MOISTURE ABSORBED
13	48	6.88	6.91	0.436	0.465
14		6.09	6.11	0.328	
15		5.73	5.76	0.522	
16		5.22	5.25	0.575	
17	96	6.39	6.43	0.626	0.624
18		6.23	6.27	0.642	
19		5.69	5.73	0.703	
20		5.73	5.76	0.524	
21	196	6.02	6.07	0.830	0.765
22		6.04	6.09	0.828	
23		6.25	6.29	0.640	
24		6.58	6.63	0.760	

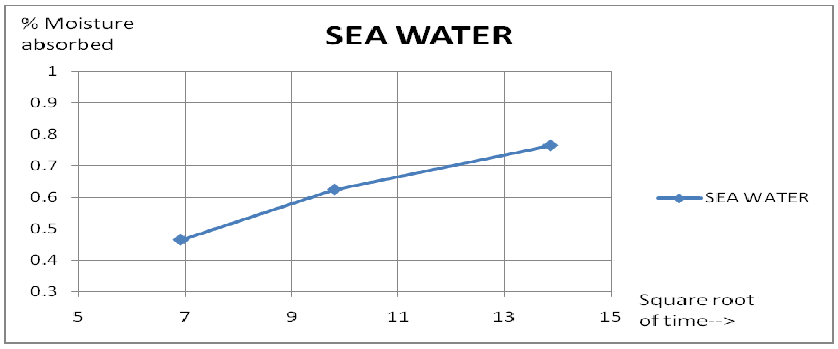
TABLE 5.3 SAMPLES IMMERSED IN 3.2% NaCl SOLUTION

SPECIMEN NO:	HOURS OF 3.2% NaCl SOLUTION IMMERSION (hrs)	INITIAL WEIGHT (gm)	FINAL WEIGHT (gm)	% MOISTURE ABSORBED	Avg. % MOISTURE ABSORBED
25	48	5.80	5.83	0.517	0.543
26		6.17	6.21	0.648	
27		6.41	6.44	0.468	
28		5.54	5.57	0.541	
29	96	5.75	5.80	0.870	0.772
30		6.16	6.20	0.649	
31		5.90	5.95	0.847	
32		5.77	5.81	0.693	
33	192	6.19	6.25	0.969	0.950
34		6.10	6.16	0.984	
35		6.06	6.12	0.990	
36		5.83	5.88	0.858	

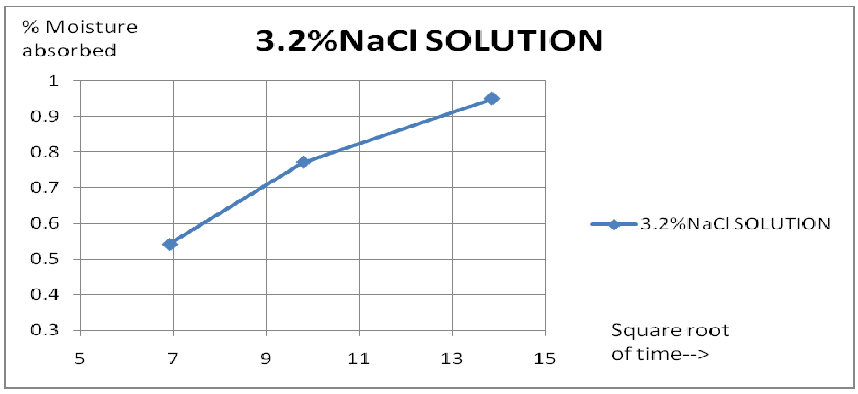
GRAPH 5.1 MOISTURE CONTENT VS SQUARE ROOT OF TIME IN DISTILLED WATER



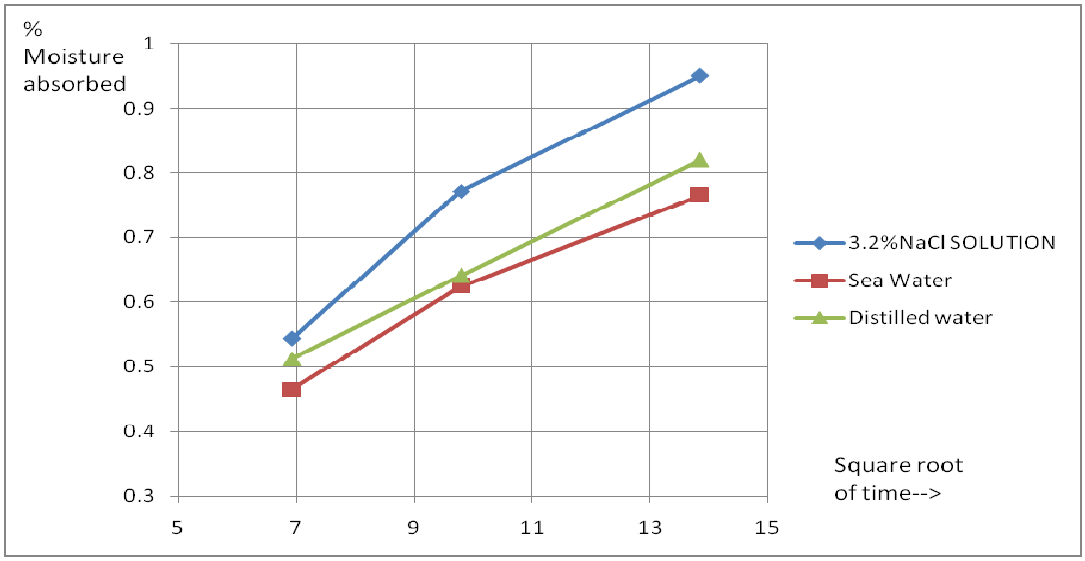
GRAPH 5.2 MOISTURE CONTENT VS SQUARE ROOT OF TIME IN SEA WATER



GRAPH 5.3 MOISTURE CONTENT VS SQUARE ROOT OF TIME IN 3.2% NaCl SOLUTION



GRAPH 5.4 MOISTURE CONTENT VS SQUARE ROOT OF TIME IN DISTILLED WATER, SEA WATER AND 3.2% NaCL SOLUTION



Graphs 5.1, 5.2, 5.3 & 5.4 show variation of weight gain of the specimen Vs square root of time for glass fiber epoxy compounds. The diffusivity for the specimens in the salt water is much higher. This implies that there is either preferential diffusion of NaC1 molecules or that the presence of salt creates an additional capacity in the specimen to accommodate more water. The diffusivity for the specimens in sea water is lowest due to presence of bulky compounds.

Generally glass fiber epoxy composites deviate from linearity, this deviation from linearity implies relaxation from Fickian behavior, and this can be attributed to the fact that moisture may get accumulated in the interface without changing the concentration.

We find that the initial rate of moisture absorption is high. The absorption is Fickian in nature (it obeys FICK'S second law). But gradually the absorption rate decreases as is

evident from the decreasing slope of the curve. This happens due to saturation of the matrix.

Among the three mediums the behavior in distilled water shows minimum deviation from linearity. In sea water and 3.2% NaCl solution the rate of water absorption is initially high than decreases as evident from the decrease in slope may be due to saturation of the matrix or presence of salts which hinder the diffusion process. The bulky nature of salts present in sea water with their osmotic effects is probably the cause of decrease in the rate of moisture absorption with time.

5.2 EFFECT OF DIFFERENT ENVIRONMENTS ON ILSS WITH TIME

TABLE 5.4 ILSS DEGRADATION FOR DISTILLED WATER IMMERSION AFTER DIFFERENT TIME INTERVALS:-

SPECIMEN NO:	HOURS OF DISTILLED WATER IMMERSION (hrs)	STRESS AT YIELD (MPa)	LOAD AT YIELD (KN)	ILSS (MPa)	Avg. ILSS (MPa)
1	48	250.3	2.813	29.034	28.379
2		243.5	2.971	28.530	
3		229.6	2.603	26.909	
4		255.9	2.789	29.043	
5	96	231.2	2.856	27.752	27.387
6		217.2	2.866	27.044	
7		225.2	3.032	28.235	
8		223.1	2.884	26.518	

9	**192**	**203.4**	**2.327**	**24.239**	**24.189**
10		**189.4**	**2.442**	**23.329**	
11		**191.6**	**2.207**	**22.166**	
12		**223.3**	**2.783**	**27.021**	

TABLE 5.5 ILSS DEGRADATION FOR SEA WATER IMMERSION AFTER DIFFERENT TIME INTERVALS:-

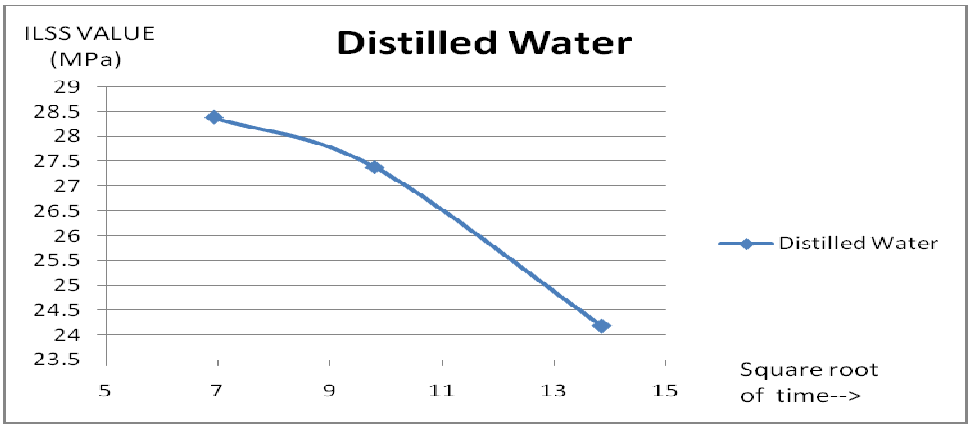
SPECIMEN NO:	HOURS OF SEA WATER IMMERSION (hrs)	STRESS AT YIELD (MPa)	LOAD AT YIELD (KN)	ILSS (MPa)	Avg. ILSS (MPa)
13	**48**	**261.7**	**2.753**	**29.740**	**28.527**
14		**220.1**	**3.007**	**26.642**	
15		**265.3**	**2.866**	**29.845**	
16		**249.3**	**2.372**	**27.879**	
17	**96**	**257.3**	**2.985**	**28.941**	**27.834**
18		**212.9**	**2.704**	**26.041**	
19		**239.3**	**3.173**	**29.714**	
20		**216.0**	**2.970**	**26.638**	
21	**192**	**201.7**	**2.433**	**24.135**	**25.957**
22		**224.4**	**2.614**	**26.630**	
23		**225.7**	**2.619**	**26.145**	
24		**217.1**	**2.900**	**26.919**	

TABLE 5.6 ILSS DEGRADATION IN 3.2% NaCl SOLUTION AFTER DIFFERENT TIME INTERVALS:-

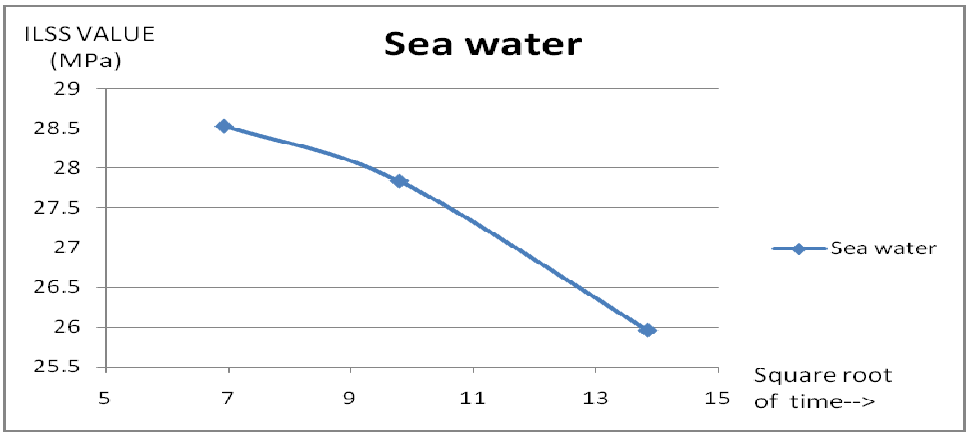
SPECIMEN NO:	HOURS OF 3.2% NaCl SOLUTION IMMERSION (hrs)	STRESS AT YIELD (MPa)	LOAD AT YIELD (KN)	ILSS (MPa)	Avg. ILSS (MPa)
25	**48**	**270.4**	**3.072**	**31.049**	**28.539**
26		**237.9**	**3.118**	**29.427**	
27		**247.5**	**3.050**	**30.240**	
28		**197.2**	**2.195**	**23.441**	

29	96	234.7	2.481	26.994	26.647
30		222.2	2.516	25.629	
31		238.0	2.716	28.242	
32		214.3	2.536	25.722	
33	192	227.9	2.633	26.175	24.086
34		203.9	2.227	23.422	
35		166.5	2.172	20.595	
36		219.4	2.513	26.151	

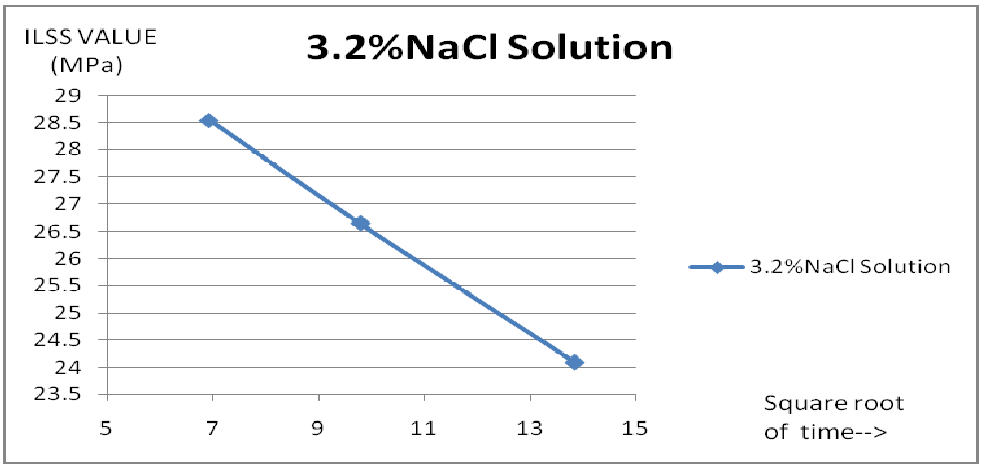
GRAPH 5.5 ILSS VALUE VS SQUARE ROOT OF TIME IN DISTILLED WATER



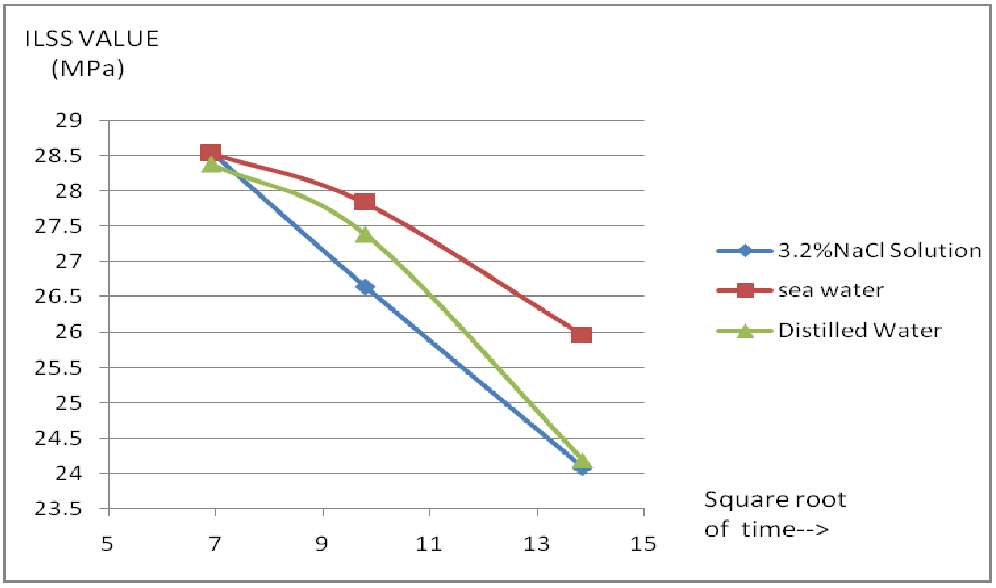
GRAPH 5.6 ILSS VALUE VS SQUARE ROOT OF TIME IN SEA WATER



GRAPH 5.7 ILSS VALUE VS SQUARE ROOT OF TIME IN 3.2% NaCl SOLUTION



GRAPH 5.8 ILSS VALUE VS SQUARE ROOT OF TIME IN DISTILLED WATER, SEA WATER AND 3.2% NaCl SOLUTION



It was found that all the solutions marginally degraded the mechanical properties, especially at higher temperature, this is mainly result of polymer hydrolysis.

As we found out that decrease in ILSS values is maximum in 3.2% NaCl solution followed by Distilled water and sea water mediums the reduction in ILSS values can be caused by water induced hydrolysis or by swelling induced micro cracking or both.

Concerning differences in result obtained by soaking the epoxy in different solutions, it has to be recognized that the amount of liquid that can diffuse into a polymer sample depend on the size of the diffusing molecules relative to the free volume available with in the polymer and also on the affinity of the diffusing molecule to specific functional groups present in the polymer .The changes in water concentration and the nature of the bound water are probably responsible for the different observed rates of polymer curing and subsequent degradations that manifest themselves as changes in strength and failure strain.

The presence of water at the interphase causes the covalent chemical bonds between the silane coupling agents and the glass surface to transform into strong physical interactions via formation of hydrogen bonds between the glass surface, water molecules and network of silane coupling agents.

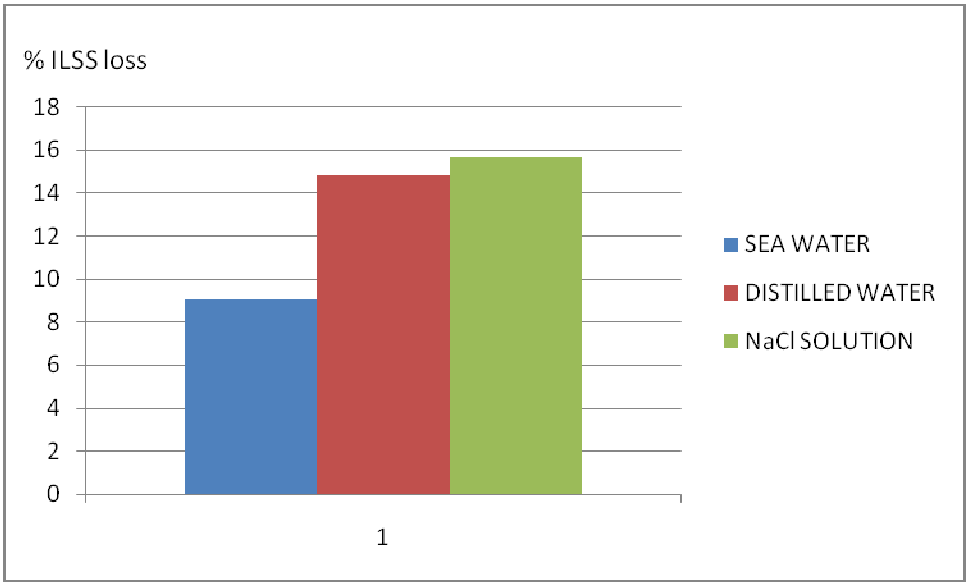
The formation of hydrogen bonds may be represented as shown below:

H-O-H + P_1 (polar group) = H-O-H----- P_1 (Single hydrogen bond)

H-O-H + P_2 (polar group) = H-O-H----- P_2 (Single hydrogen bond)

H-O-H-------P_1 + H-O-H--------P_2 = P1------H-O-H------ P_2 (Double hydrogen bond)

GRAPH 5.9 PERCENTAGE DECREASE OF ILSS VALUE IN DISTILLED WATER, SEA WATER AND 3.2% NaCl SOLUTION



The percentage loss in ILSS is maximun in NaCl solution and minimun in sea water. This may be due the highest diffusivity in NaCl solution and lowest in sea water that we found earlier.

5.3 SCANING ELECTRON MICROSCOPE RESULTS

1. FRP COMPOSITE IMMERSED IN SEA WATER FOR 8 DAYS

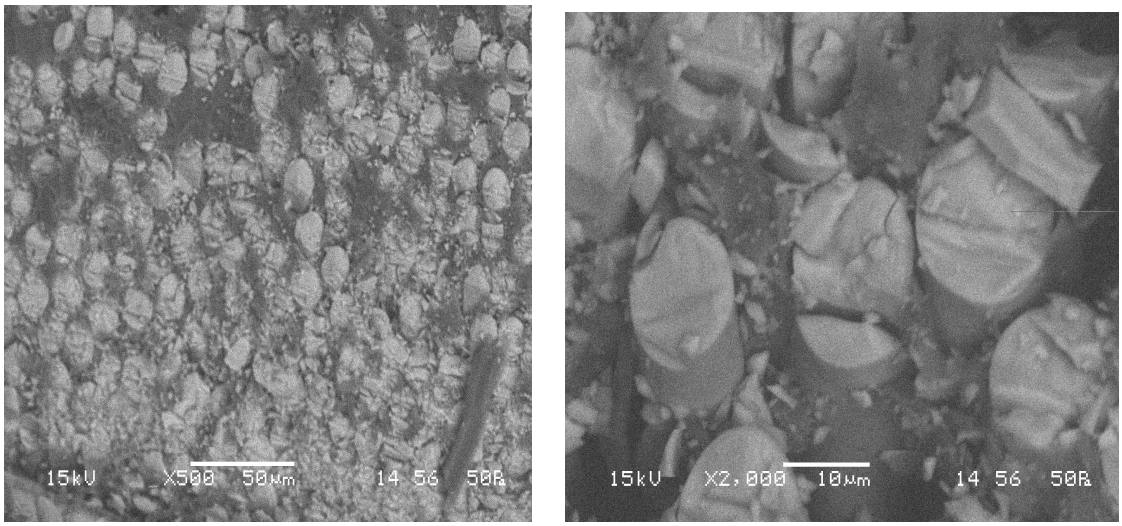


Figure 5.1 SEM Images of the Fractured Surface of specimen immersed in sea water.

Interpretation

- From the above Images, it is clear that the matrix is strongly bonded to the fibers at the interface and this result in the increase of strength and fracture is ductile.
- In the above figure we can see cause of failure is fiber breakage, thus load transference to the fibers takes place efficiently, so may be the decrease in ILSS value is minimum in sea water medium.

2. FRP COMPOSITE IMMERSED IN DISTILLED WATER FOR 8 DAYS

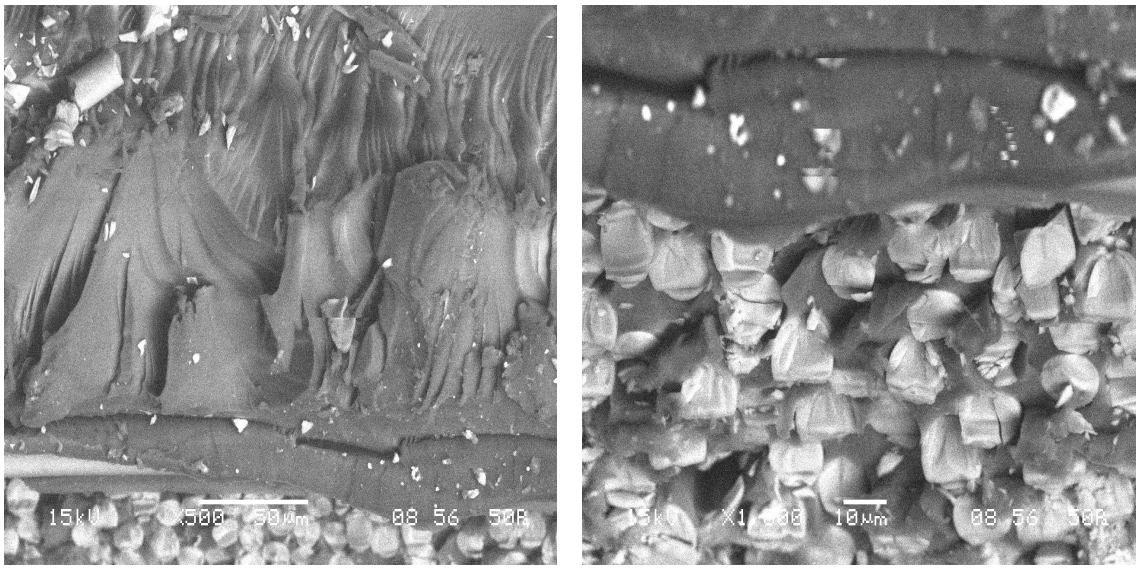


Figure 5.2 SEM Images of the Fractured Surface of specimen immersed in distilled water.

Interpretation

- From the above Images, it is clear that the matrix has squeezed due to the moisture absorption.
- As we can see cracks in the matrix region which originate from the interface, which may be the reason behind the decrease in ILSS values.

3. FRP COMPOSITE IMMERSED IN 3.2% NaCl SOLUTION FOR 8 DAYS

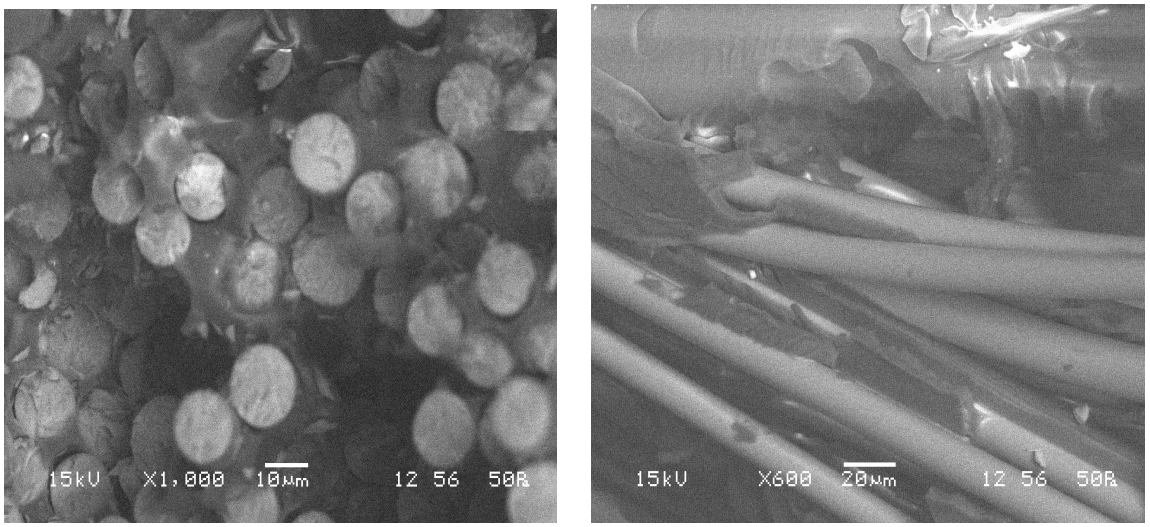


Figure 5.3 SEM Images of the Fractured Surface of specimen immersed in NaCl solution

Interpretation

- Due to moisture absorption some of the fibers have loosen contact with the matrix and thus this results in the decrease of strength. We can see much greater debonding here than the previous cases, that may be the reason for large decrease in ILSS values in case of 3.2% NaCl solution.
- We can also see matrix weakening and fiber pullout may be due polymer hydrolysis which further reduces the strength of the composite.

5.4 EFFECT OF DIFFERENT ENVIRONMENT ON ILSS WITH TIME AFTER HEATING THE SAMPLES

TABLE 5.7 ILSS DEGRADATION UNDER DISTILLED WATER WITH DIFFERENT TIME INTERVALS AFTER HEATING:-

SPECIMEN NO:	HOURS OF DISTILLED WATER IMMERSION (hrs)	STRESS AT YIELD (MPa)	LOAD AT YIELD (KN)	ILSS (MPa)	Avg. ILSS (MPa)
1	48	277.7	2.534	25.033	26.809
2		312.9	3.204	28.585	
3	96	276.6	2.643	25.623	26.329
4		301.2	2.715	27.035	
5	192	280.0	2.157	24.146	25.671
6		319.0	2.651	27.195	

GRAPH 5.10 ILSS VALUE VS SQUARE ROOT OF TIME FOR DISTILLED WATER AFTER HEATING

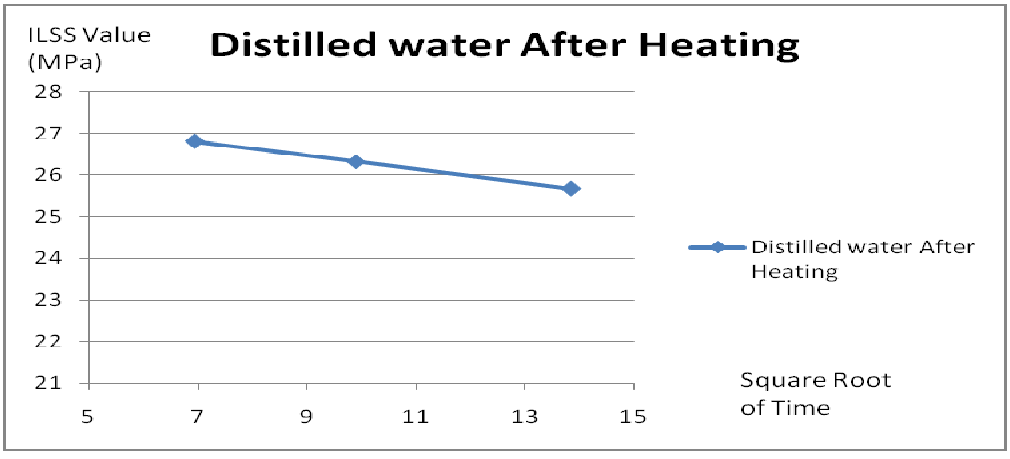


TABLE 5.7 ILSS DEGRADATION UNDER SEA WATER WITH DIFFERENT TIME INTERVALS AFTER HEATING:-

SPECIMEN NO:	HOURS OF SEA WATER IMMERSION (hrs)	STRESS AT YIELD (MPa)	LOAD AT YIELD (KN)	ILSS (MPa)	Avg. ILSS (MPa)
7	48	309.6	2.723	27.863	27.177
8		292.7	2.813	26.491	
9	96	326.6	2.790	29.552	26.576
10		269.7	2.229	23.599	
11	192	320.1	2.668	27.126	26.709
12		299.6	2.584	26.292	

GRAPH 5.11 ILSS VALUE VS SQUARE ROOT OF TIME FOR SEA WATER AFTER HEATING

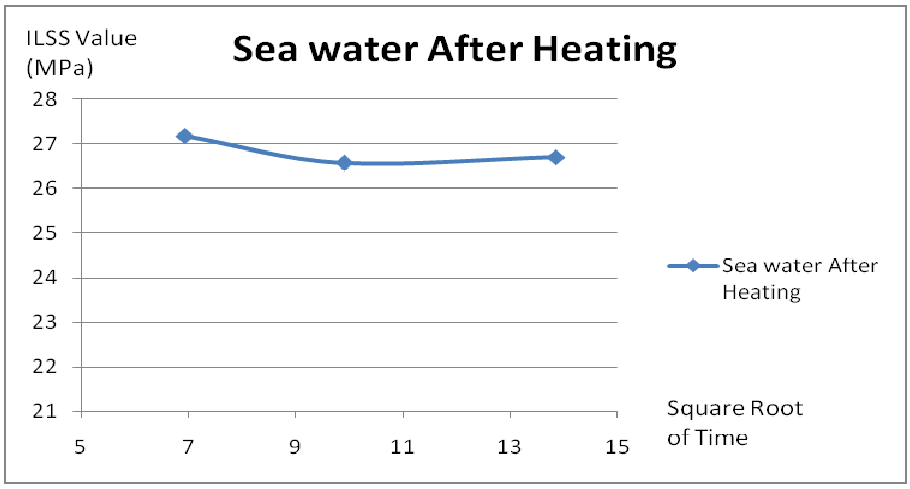
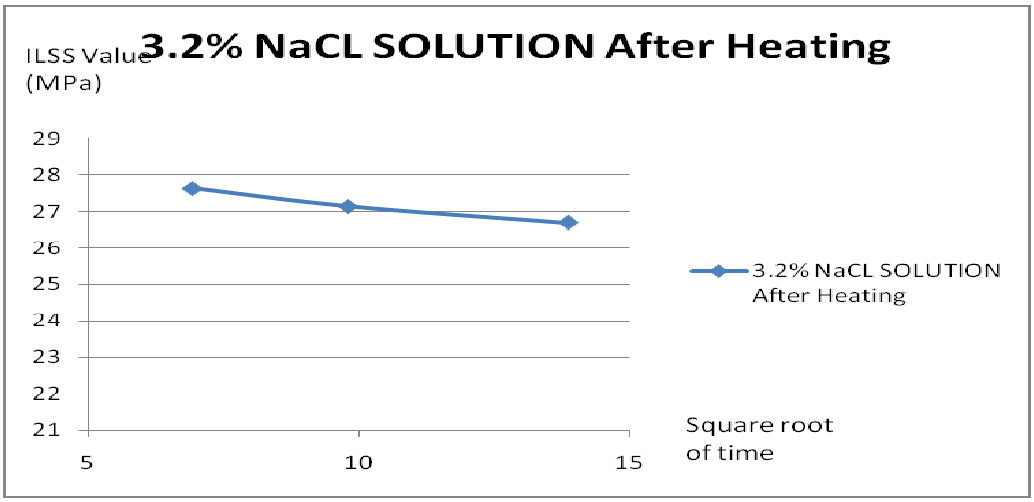


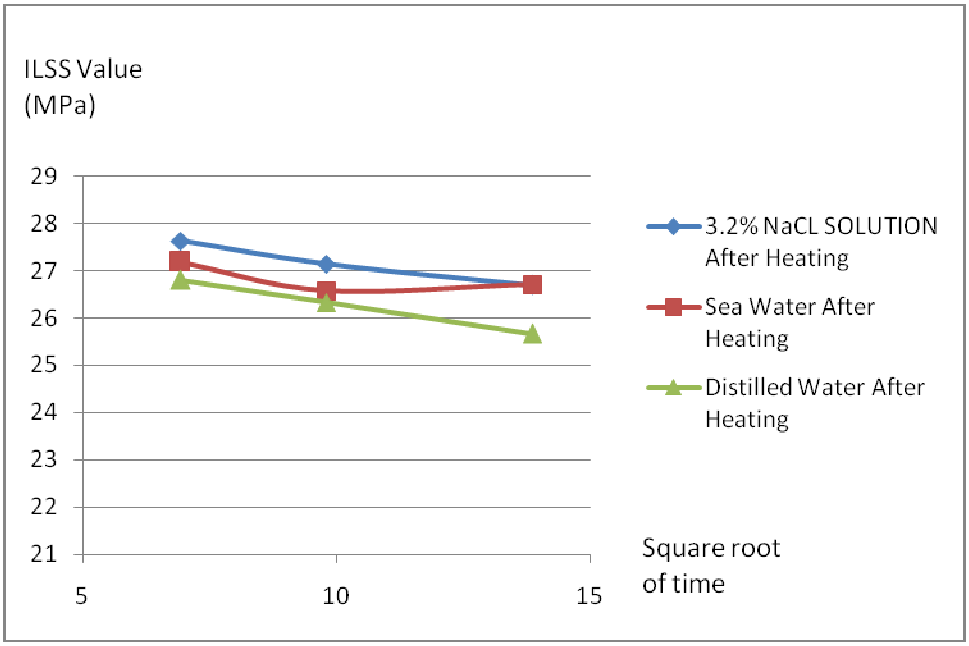
TABLE 5.7 ILSS DEGRADATION UNDER 3.2% NaCl SOLUTION WITH DIFFERENT TIME INTERVALS AFTER HEATING:-

SPECIMEN NO:	HOURS OF 3.2% NaCl SOLUTION IMMERSION (hrs)	STRESS AT YIELD (MPa)	LOAD AT YIELD (KN)	ILSS (MPa)	Avg. ILSS (MPa)
13	48	307.7	2.576	26.577	27.632
14		323.7	2.823	28.686	
15	96	312.1	2.289	26.065	27.138
16		304.9	2.828	28.211	
17	192	294.7	2.404	26.667	26.691
18		298.0	2.874	26.715	

GRAPH 5.12 ILSS VALUE VS SQUARE ROOT OF TIME IN 3.2% NaCL SOLUTION



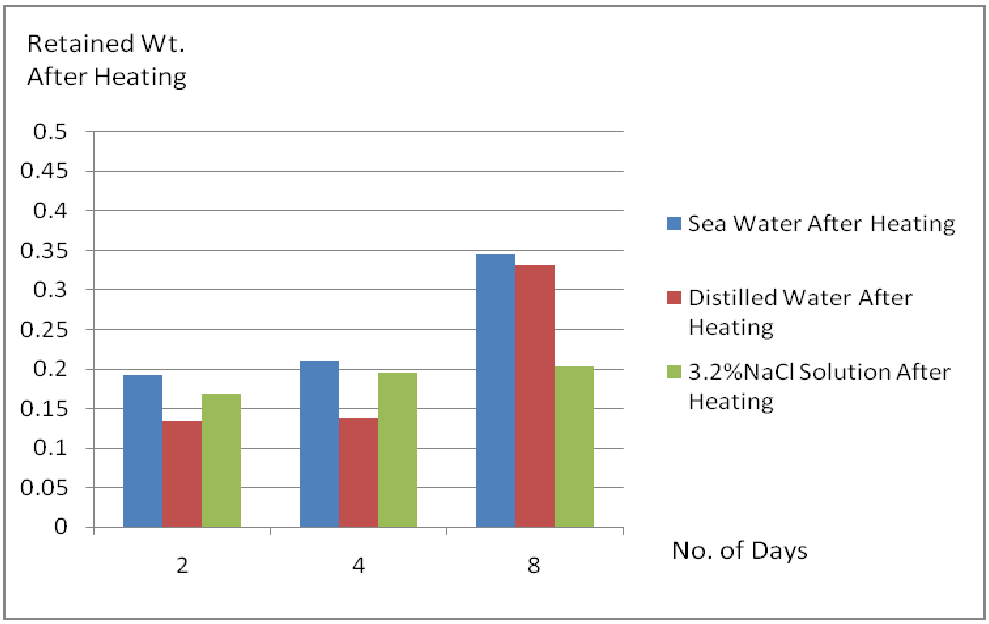
GRAPH 5.13 ILSS VALUE VS SQUARE ROOT OF TIME IN DISTILLED WATER, SEA WATER AND 3.2% NaCL SOLUTION AFTER HEATING



Interpretation

- In genral we can see from the above graphs, the decrease in ILSS values of the hygrothermally treated samples after heating is very less, this can be attributed to the curing that might have occurred during heating, which increased the strength.In case of sea water we can even see an increase in The ILSS value with time.
- The reduction in the ILSS values which shows degradation of mechanical properties is due to the salts present in the flaws of the matrix which become the potential sources of crack nucleation and chemically combined moisture which the matrix retains causing the weakening of the fiber matrix bonds**.**

5.5 WEIGHT RETAINED IN THE SAMPLES



The main component of residue after immersion test is unsaturated polyester [weight and curing]. Unsaturated polyester was used as the binder in manufacture in order to form the glass-fiber material. The characteristics of the binder were a little different from those of the matrix resin despite their being the same unsaturated polyester. It is hypothesized that the binder dissolves into water at the fiber/matrix interface. In sea water and salt solution, some salts have diffused into the matrix by osmosis which increases the weight of the samples after heating.

5.6 Variation of Glass Transition Temperature in different environments

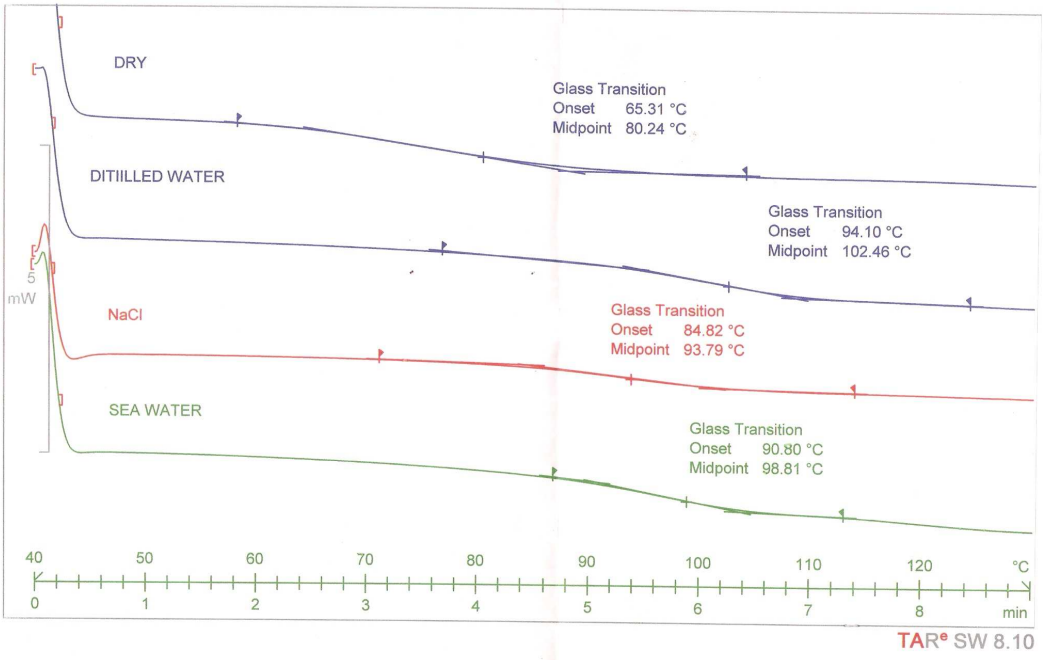


Fig no.5.4 DSC curve of dry specimen and specimen immersed in distilled water, 3.2% NaCl solution and sea water.

T_g variation is represented in Fig. no. 5.4, this represent the data for dry sample i.e. the sample without hydrothermal treatment and samples immersed in distilled water and NaCl solution and sea water respectively for eight days. There seems to be an experimental lapse in case of dry sample which shows the minimum T_g 65.3˚C.The sample with distilled water shows the maximum T_g 94.1˚C this is because of hydrogen double bond formation which delays the setting of transition resulting in higher T_g. The sample immersed in NaCl solution shows a T_g of 84.82 ˚C and that in sea water shows a T_g of 90.80 ˚C. This is because of hydrogen double bond formation which has delayed the transition however when compared with distilled water it clearly shows that the NaCl present in the sea water and NaCl solution has interfered with the modification of the

transition temperature, however the extent of modification and the mechanism needs further investigation.

Chapter 6

CONCLUSION

6.1 CONCLUSION

Glass fiber reinforced composite when exposed to degrading atmosphere like 3.2% NaCl solution, sea water and distilled water, generally decreases the mechanical properties.

The diffusivity was found maximum in case of 3.2% NaCl solution and minimum in sea water with distilled water showing intermediary results. The rate of diffusion is initially higher than gradually decreases due to saturation of matrix.

Again, the maximum decrease in ILSS values was found in case of 3.2% NaCl solution and minimum in sea water with distilled water showing intermediary results. As decrease in ILSS depends directly on moisture absorption.

SEM photographs of the fractured surface in case of 3.2% NaCl solution showed much greater debonding and fiber pull-outs than distilled water where matrix cracking seems to be the major cause. The matrix is least affected in sea water solution.

Specimen subjected to heating after immersion in these mediums showed some improvement in their ILSS values which is probably due to the curing that might have taken place curing.

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